

# Superconductivity at 41 K and its competition with spin-density-wave instability in layered $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$

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A series of layered  $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$  compounds with  $x=0$  to 0.20 are synthesized by solid state reaction method. Similar to the  $\text{LaOFeAs}$ , the pure  $\text{CeOFeAs}$  shows a strong resistivity anomaly near 145 K, which was ascribed to the spin-density-wave instability. F-doping suppresses this instability and leads to the superconducting ground state. Most surprisingly, the superconducting transition temperature could reach as high as 41 K. The very high superconducting transition temperature strongly challenges the classic BCS theory based on the electron-phonon interaction. The very closeness of the superconducting phase to the spin-density-wave instability suggests that the magnetic fluctuations play a key role in the superconducting pairing mechanism. The study also reveals that the Ce 4f electrons form local moments and ordered antiferromagnetically below 4 K, which could coexist with superconductivity.

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The recent discovery of superconductivity with transition temperature of 26 K in  $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$  system[1] has generated tremendous interest in the scientific community. Except for a relatively high transition temperature, the system displays many interesting properties. Among others, the presence of competing ordered ground states is one of the most interesting phenomena[2]. The pure  $\text{LaOFeAs}$  itself is not superconducting but shows an anomaly near 150 K in both resistivity and dc magnetic susceptibility.[1] This anomaly was shown to be caused by the spin-density-wave (SDW) instability.[2] Electron-doping by F suppresses the SDW instability and recovers the superconductivity. Here we show that similar competing orders exist in another rear-earth transition metal oxypnictide  $\text{Ce}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ . Most surprisingly, the superconducting transition temperature in this system could reach as high as 41 K. Except for cuprate superconductors,  $T_c$  in such iron-based compounds has already become the highest.

The very high superconducting transition temperature has several important implications. First, the  $T_c$  value has already reached the well-accepted limit value of classic BCS theory[3, 4]. Considering the small carrier density and rather weak electron-phonon coupling estimated from first-principle calculations[5, 6], the observation result strongly challenges the BCS theory based on the electron-phonon interaction. Second, the rare-earth Ce-based compounds usually show hybridization between localized f-electrons and itinerant electrons. This often leads to a strong enhancement of carrier effective mass at low temperature. Even for 4d transition metal oxypnictide with the same type of structure, a recent report indicates that the electronic specific heat coefficient of Ce-based  $\text{CeORuP}$  ( $\gamma=77$  mJ/mol K<sup>2</sup>) is 20 times higher than the value of La-based  $\text{LaORuP}$  ( $\gamma=3.9$  mJ/mol K<sup>2</sup>)[7]. The hybridization also tends to cause various ordered states at low temperature, like ferromag-

netic (FM) or antiferromagnetic (AFM) ordering. Although superconducting state could occur in Ce-based materials, the superconducting transition temperature is usually very low. The highest superconducting transition temperature is only 2.3 K achieved in  $\text{CeCoIn}_5$ [8]. The extremely high superconducting transition temperature obtained here on  $\text{Ce}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$  offers an opportunity to examine the role played by Ce 4f electrons. Third, the superconducting phase is very close to the spin-density-wave instability. This indicates that the magnetic fluctuations plays a key role in the superconducting pairing mechanism.

A series of layered  $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$  compounds with  $x=0, 0.04, 0.08, 0.12, 0.16$  and 0.20 are synthesized by solid state reaction method using CeAs, Fe,  $\text{CeO}_2$ ,  $\text{CeF}_3$ ,  $\text{Fe}_2\text{As}$  as starting materials. CeAs was obtained by reacting Ce chips and As pieces at 500 °C for 15 hours and then 850 °C for 5 hours. The raw materials were thor-

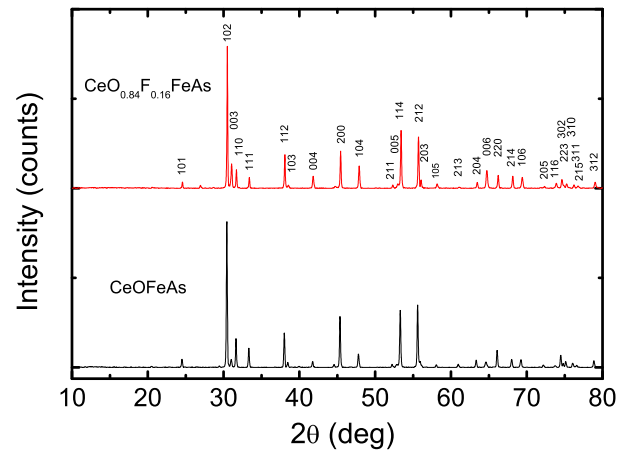


FIG. 1: (Color online) X-ray powder diffraction patterns of the pure  $\text{CeOFeAs}$  and  $\text{CeO}_{0.84}\text{F}_{0.16}\text{FeAs}$  compounds.

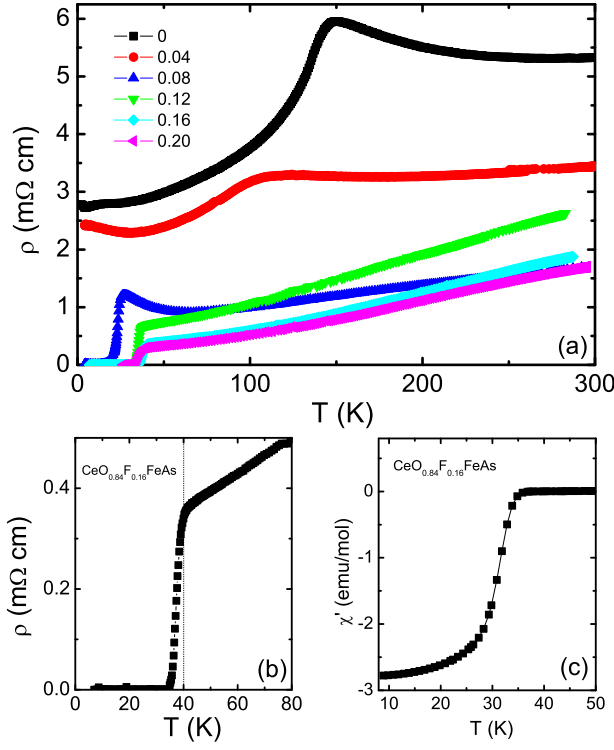


FIG. 2: (Color online) (a) The electrical resistivity vs temperature for a series of  $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$ . (b) T-dependent resistivity in an expanded region for  $x=0.16$  sample. The superconducting transition with sharp onset temperature at 41 K is seen. (c) Real part of T-dependent ac magnetic susceptibility.

oughly mixed and pressed into pellets. The pellets were wrapped with Ta foil and sealed in an evacuate quartz tube. They were then annealed at 1150  $^{\circ}\text{C}$  for 50 hours. The resulting samples were characterized by a powder X-ray diffraction(XRD) method with Cu  $K\alpha$  radiation at room temperature. Almost pure phase was achieved for those samples. The XRD patterns for the parent  $x=0$  and  $x=0.16$  compounds are shown in Fig. 1, which could be well indexed on the basis of tetragonal  $\text{ZrCuSiAs}$ -type structure with the space group  $P4/nmm$ . The lattice parameters for the parent and  $x=0.16$  compounds obtained by a least-square fit to the experimental data are  $a=3.996$   $\text{\AA}$ ,  $c=8.648$   $\text{\AA}$ , and  $a=3.989$   $\text{\AA}$ ,  $c=8.631$   $\text{\AA}$ , respectively. Compared to the undoped phase  $\text{CeOFeAs}$ , the apparent reduction of the lattice volume upon F-doping indicates a successful chemical substitution.

Standard 4-probe dc resistivity and ac susceptibility measurements were performed down to 1.8 K in a Physical Property Measurement System(PPMS) of Quantum Design company. Figure 2 (a) shows the temperature dependence of the resistivity. The pure  $\text{CeOFeAs}$  sample has rather high dc resistivity value. The resistivity increases slightly with decreasing temperature, but below roughly 145 K, the resistivity drops steeply. After F-doping, the overall resistivity decreases and the 145 K anomaly shifts

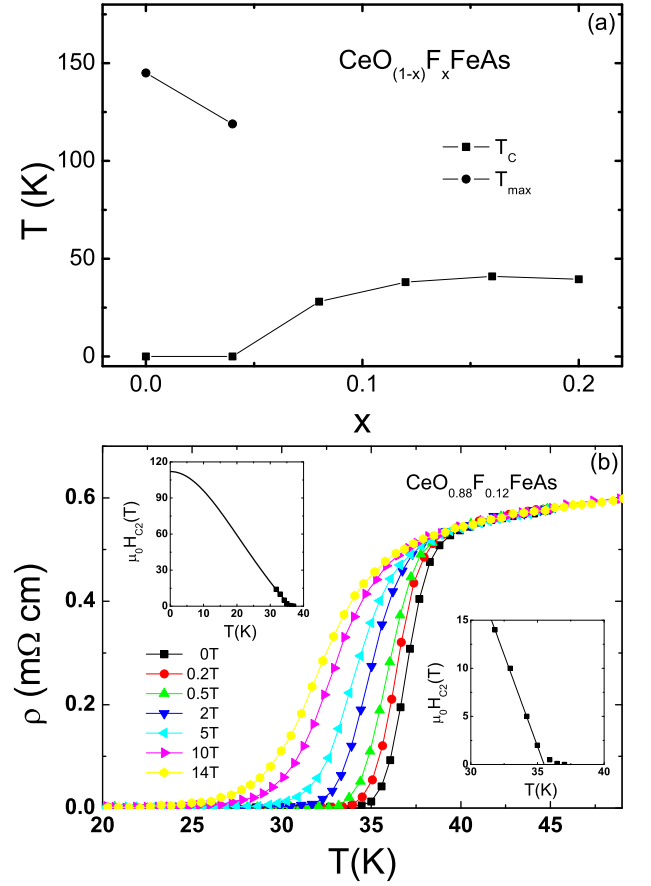


FIG. 3: (Color online) (a) The phase diagram showing the anomaly (circle) and superconducting transition (square) temperatures as a function of F content. (b) The resistivity vs temperature curves under several selected magnetic fields. The lower inset shows the temperature dependence of upper critical field. The solid line indicates the slope. The upper inset is a fit to the equation described in the text.

to the lower temperature and becomes less pronounced. At higher F-doping, the anomaly disappears and a superconducting transition occurs. The highest  $T_c=41$  K is obtained at  $x=0.16$ , which can be seen clearly from an expanded plot of the temperature-dependent resistivity curve.  $T_c$  drops slightly with further F-doping. The bulk superconductivity in F-doped  $\text{CeOFeAs}$  is confirmed by ac magnetic susceptibility measurements. Figure 2 (c) shows the the real part  $\chi'$  of ac susceptibility in a temperature range near  $T_c$  for the  $x=0.16$  sample. Figure 3 (a) is the phase diagram showing the resistivity anomaly (circle) and superconducting transition (square) temperatures as a function of F content.

An important parameter to characterize superconductivity is the upper critical field  $H_{c2}(0)$ . In our earlier study on  $\text{LaO}_{0.9}\text{F}_{0.1-\delta}\text{FeAs}$  superconductor with an onset  $T_c=26$  K, we already found a rather high upper critical field  $H_{c2}(0)\sim 54$  T [9]. Here we would expect much higher  $H_{c2}(0)$  in Ce-based compounds owing to their sub-

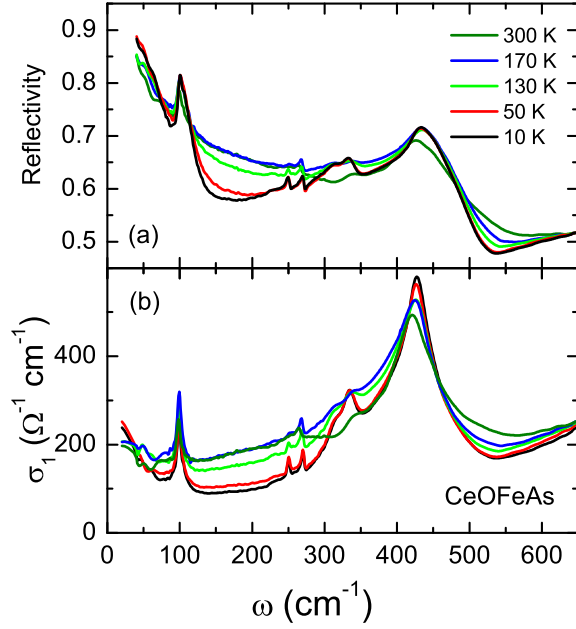


FIG. 4: (Color online) The reflectance (a) and conductivity (b) spectra in the far-infrared region at different temperatures for the pure CeOFeAs sample.

stantially higher  $T_c$ . For this purpose, we measured the temperature-dependent resistivity of a  $x=0.12$  sample with  $T_c$  onset close to 40 K under different magnetic fields. As shown in Fig. 3 (b),  $T_c$  was suppressed only by several Kelvins at 14 T (which is the highest magnetic field available in our PPMS system). The critical field vs. temperature ( $H_{c2}$ - $T$ ) curve near  $T_c$  was plotted in the lower inset. Here the  $T_c(H_{c2})$  is defined as a temperature at which the resistivity falls to half of the normal state value (middle transition). As described in our earlier work[9], the  $H_{c2}(0)$  could be extracted from two different methods: (i) by using the Werthamer-Helfand-Hohenberg (WHH) relation,  $H_{c2}(0) \approx 0.691 |dH_{c2}/dT| \times T_c$ , with a critical-field slope near  $T_c$  (being about -3.86 T/K), (ii) from a fit to the equation  $H_{C2}(T) = H_{C2}(0) [1 - (T/T_c)^2] / [1 + (T/T_c)^2]$ , as shown in the upper inset. Then, we obtain  $H_{c2}(0) \sim 107$  T and 112 T, respectively. We remark here that those rather high estimated values of  $H_{c2}(0)$  are still at the lower limit for the upper critical field, because the criteria for the  $T_c(H_{c2})$  in above analysis is defined at the middle transition, not at the onset transition temperature, which actually shows smaller shift with field. Additionally, the multiple bands effect was not taken into account.

The resistivity behavior of the pure CeOFeAs is very similar to that of LaOFeAs, except for the difference that a resistivity upturn was observed in the later compound at lower temperature. As we demonstrated earlier, the anomaly at 150 K is caused by spin-density-wave insta-

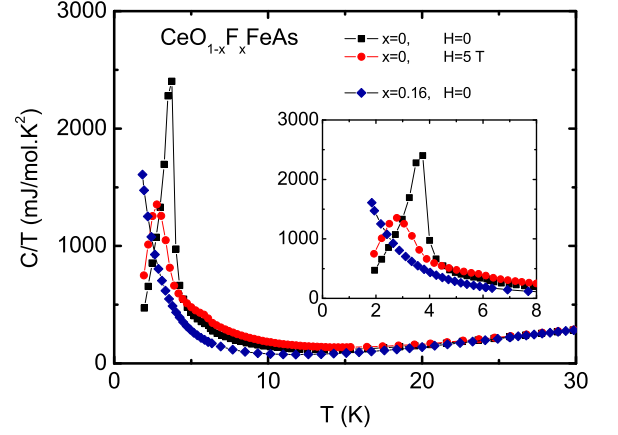


FIG. 5: (Color online) The plot of  $C/T$  vs.  $T$  for the pure CeOFeAs sample at  $H=0$  and 5T, and the 16% F-doped  $\text{CeO}_{0.84}\text{F}_{0.16}\text{FeAs}$  sample at  $H=0$ , respectively. The inset shows the plot in an expanded low temperature range.

bility, and a gap opens below the transition temperature due to the Fermi surface nesting[2]. To confirm the same origin for the anomaly, we performed infrared measurement on Bruker 66v/s spectrometer in the frequency range from  $40 \text{ cm}^{-1}$  to  $15,000 \text{ cm}^{-1}$  at different temperatures, and derived conductivity from Kramers-Kronig transformations. Figure 4 shows the reflectance and conductivity spectra in far-infrared region. As expected, CeOFeAs shares very similar optical response behavior as LaOFeAs. Most notably, the reflectance below  $400 \text{ cm}^{-1}$  is strongly suppressed at low frequency below the phase transition temperature, which is a strong indication for the formation of an energy gap. However, the low-frequency reflectance still increases fast towards unity at zero frequency, indicating metallic behavior even below the phase transition, being consistent with the dc resistivity measurement which reveals an enhanced conductivity. The data indicate clearly that only partial Fermi surfaces are gapped.

We noticed that, among different reported superconducting systems in such layered transition metal oxypnictides, the  $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$  and  $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$  systems share remarkably similar phenomenon: the presence of competing ground states. When the SDW order is destroyed by electron doping, superconductivity could occur at a much higher temperature. This gives a hint where to search for materials with potentially higher  $T_c$ . The interplay between superconductivity and spin-density-wave instability thus is of central interest in those systems.

To get insight into whether the rare-earth element Ce 4f electrons hybridize with the itinerant Fe 3d electrons at low temperature, we measured the low-T specific heat. To our surprise, another magnetic ordering was revealed in those Ce-based samples. Fig. 5 shows the plot of  $C/T$  as a function of temperature for pure CeOFeAs at  $H=0$

and 5T, and 16% F-doped  $\text{CeO}_{0.84}\text{F}_{0.16}\text{FeAs}$  at  $H=0$ , respectively. For non-superconducting  $\text{CeOFeAs}$ , a sharp  $\lambda$ -shape peak at 3.7 K is observed under zero magnetic field. The peak shifts to 2.8 K under a magnetic field of 5 T. This clearly indicates that a long-range antiferromagnetic ordering transition occurs at low temperature. There is a very weak effect in  $dc$  resistivity at the AFM transition temperature. For  $\text{LaOFeAs}$  without rare earth 4f electrons, there is no such specific heat anomaly at low temperature[2], indicating unambiguously that the AFM transition for  $\text{CeOFeAs}$  is originated from the ordering of Ce 4f moments. No significant enhancement of electronic specific coefficient is observed from the high T specific heat. For the 16% F doped superconducting sample, we also observe the onset signature of the AFM transition down to 1.8K, the lowest measured temperature. The AFM transition must occur below this temperature. The data strongly suggest that the high-temperature superconductivity coexists with the AFM ordering of Ce 4f local moments. This coexistence implies that the exchange interaction between the Ce 4f moments and the itinerant Fe 3d electrons is very weak. So, there is no appreciable mixing or hybridization between them in the present systems.

To summarize, we have synthesized a series of rare-earth based transition metal oxypnictide  $\text{CeO}_{1-x}\text{F}_x\text{FeAs}$  compounds. The superconducting transition temperature could be as high as 41 K. This very high superconducting transition temperature strongly challenges the pairing mechanism based on the electron-phonon interaction. Similar to the  $\text{LaOFeAs}$ , the pure  $\text{CeOFeAs}$  shows a strong resistivity anomaly near 145 K, which was ascribed to the spin-density wave instability. F-doping suppresses this instability and leads to the superconducting ground state with rather high  $T_c$ . The very interesting interplay between the superconducting phase and the spin-density-wave instability strongly suggests that

the magnetic fluctuations play a key role in the superconducting pairing mechanism. Furthermore, the study reveals that the Ce 4f electrons form local moments and ordered antiferromagnetically below 4 K which could coexist with superconductivity.

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Note added: After we completed this work, we learnt an independent work on another rare-earth Sm-based  $\text{SmFeAsO}_{1-x}\text{F}_x$  ( $x=0.1$ ) by Chen et al., arXiv:0803.3603v1.

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